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14. ABSTRACT We have completed a three-year program of research into the properties of nitrogen-rich heterocyclic compounds, all nitrogen compounds and silicon carbide clusters with adatoms. The research projects all include a very strong blend of experiment and state-of-the-art theory, obtaining structural and thermochemical properties of unusual and unstable species. The experimental approaches include anion photoelectron spectroscopy and detailed investigations of ion-molecule reactions using flowing afterglow and drift tube reactors. These techniques together provide complementary information that yields quantitative thermochemical information on very unstable species. The ability of the flow reactor to study minute quantities of ions also allows the investigation of speculative, possibly low-yield pathways to these energetic molecules. Specifically, we are studying the ion chemistry and thermochemical properties of a number of nitrogen-rich heterocyclic compounds and their radicals. Time-resolved photoelectron imaging measurements yield new insight into the ultrafast dynamics.					
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# AFOSR Final Performance Report

F49620-02-1-0371

**Thermochemistry and Dynamics of Reactive Species:  
Nitrogen-rich Compounds, Metals, and SiC clusters in Free and Solvated Environments**

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31 October, 2005

## Objectives

The objectives of this research program remain the same as before: obtaining fundamental thermochemical and dynamical data on reactive species

## Status of Effort

This report summarizes our activities over the period from August 1, 2002 through July 31, 2005. This has been a collaborative experimental/theoretical project with the first objective to obtain experimental data, the second to obtain accurate *ab initio* anion and neutral cluster structure calculations, and the third objective to obtain dynamical information on the stability of these species. Both experimental and theoretical techniques have needed development in order to carry out these objectives. During the past year, our primary emphasis has been placed on a detailed study of the stability of the pyrrolyl radical and the pseudo Jahn-Teller distortions and instabilities of this radical. Other important studies have included a detailed characterization of collision-induced dissociation, comparing experimental results in a flowing afterglow with those obtained under single collision beam conditions. Finally, we have begun investigations of molecular dynamics using a charge reversal machine, and we have developed a new photoelectron imaging spectrometer, which will enable unique real-time observations of reactive processes.

Progress in each of the areas is briefly summarized in the following sections.

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## Ion Chemistry

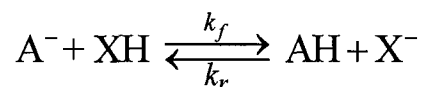
The ion reactions and mechanisms research program has focussed on the gas phase ion reactions, mechanisms, kinetics, and thermochemistry of a wide variety of organic and inorganic species, utilizing the flowing afterglow-selected ion flow tube-triple quadrupole technique. This powerful and versatile approach has allowed the study of the chemistry of many nitrogenous ions and compounds. An arsenal of ionization and reaction methods generates a wide array of ionic precursors; these methods included ionization by electron impact, microwave discharge, and several dc discharge methods; additional flexibility is provided by synthetic ion-molecule chemistry within the source region and collision-induced dissociation of ionic species.

An important feature of this reactor is its extreme sensitivity and the ability to determine reaction rates and mechanisms with ion intensities several orders of magnitude too low to be easily utilized in the negative ion photoelectron spectroscopy apparatus. By first carrying out reactions and identifying mechanisms here, we can optimize ion production for subsequent anion photoelectron spectroscopic studies. It is the combination of these two sets of data that provides the deepest insight and most detailed thermochemical information.

The investigations will provide basic thermochemical information on a number of important nitrogen heterocycles, systems of considerable utility and yet virtually unstudied. Further, we will utilize some unique ion chemistry, including translational activation, to attempt to produce some small molecules with energetic nitrogen components. Wherever possible, these kinetic measurements will be coupled both with photoelectron spectroscopy and state of the art theory.

## Experimental

Gas phase acidities of azole compounds were determined using a tandem flowing afterglow-selected ion flow tube (FA-SIFT) instrument. The forward ( $k_f$ ) and reverse ( $k_r$ ) rate coefficients were measured at 298 K for proton transfer reactions between azole (AH) and a reference acid (XH).



The reactant anions ( $A^-$  and  $X^-$ ) were generated in the source flow tube using  $HO^-$  deprotonation of the corresponding neutrals, AH and XH. The ions were mass selected and injected into the second flow tube containing helium (0.5 Torr), where they were thermally equilibrated with the buffer gas before undergoing proton transfer reactions with added reagents. The ratio of the rate coefficients gives the proton-transfer equilibrium constant  $K_{\text{equil}}$  ( $\equiv k_f/k_r$ ). When the acidity of the reference acid is known,  $\Delta_{\text{acid}}G_{298}(\text{XH})$ , the acidity of the azole molecule is extracted from

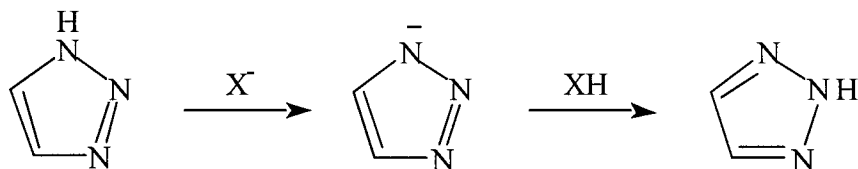
$$\Delta_{\text{acid}}G_{298}(\text{AH}) - \Delta_{\text{acid}}G_{298}(\text{XH}) = RT \ln K_{\text{equil}}$$

The gas phase acidity  $\Delta_{\text{acid}}G_{298}(\text{AH})$  is the free energy change for the process  $\text{AH} \rightarrow A^- + H^+$ . The value is converted to the enthalpy of deprotonation  $\Delta_{\text{acid}}H_{298}(\text{AH})$  using the entropy term ( $T\Delta S$ ) as derived from Gaussian 98 computations at the B3LYP/6-311++G\*\* level of theory.

The acidity for pyrrole was determined from an equilibrium measurement with methanethiol ( $\text{CH}_3\text{SH}$ ). Acidities for pyrazole and imidazole were determined with 2-methyl-2-propanethiol ( $t\text{BuSH}$ ) while formic acid ( $\text{HCOOH}$ ) was used as the reference acid for 1,2,4-triazole. Beside pyrrole, the higher azoles are solid materials and have poor vapor pressures. They were thus preheated and entrained in a stream of helium, at regulated yet unknown flow rates, into the SIFT instrument. The reverse rate coefficients ( $\text{AH} + X^- \rightarrow A^- + \text{XH}$ ) for the less volatile azoles were measured in the following manner: Given a constant flow of AH in the second flow tube, semi-logarithmic depletions were measured alternately for SIFT-injected  $HO^-$  and  $X^-$  ions in order to extract the relative reaction rates. Based on an assumption that the exothermic proton transfer reaction  $\text{AH} + HO^- \rightarrow A^- + \text{H}_2\text{O}$  proceeds at a 90% efficiency with respect to the calculated collision rate, the rate coefficient for  $\text{AH} + X^-$  was obtained accordingly. This assumption was justified by a separate measurement of the pyrrole +  $HO^-$  reaction in comparison with the calculated collision rate.

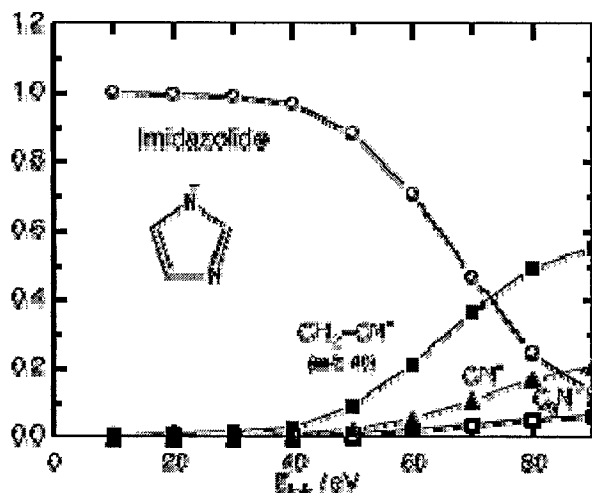
Our computations along with reported heats of formation indicate that proton-transfer equilibrium cannot be established for some azoles, *i.e.*, 1H-1,2,3-triazole and 1H-tetrazole. As

shown in the case of triazole, deprotonation with  $X^-$  produces the corresponding triazolide anion, which gets re-protonated by  $XH$  into the more stable, 2H structure.

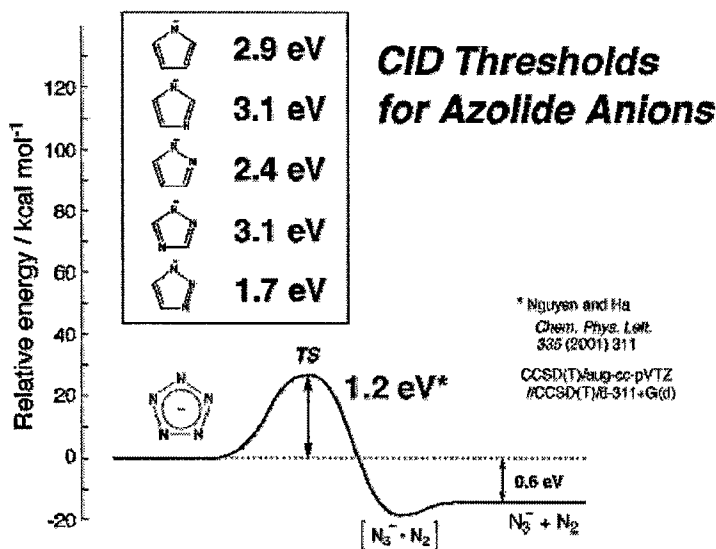


For these azoles, therefore, we used several reference acids to bracket the proton affinities for the deprotonated anions:  $A^- + XH \rightarrow AH + X^-$ . This effectively determines the ranges of gas phase acidity for the 2H azoles. For comparison, similar acidity bracketing experiments were performed for pyrrolide and pyrazolide anions.

Collision-induced dissociation (CID) experiments were conducted for deprotonated anions of pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, and tetrazole. These ions were prepared in the source flow tube and SIFT-injected into the second flow tube at varied injection potentials. Collisions with helium take place in the vicinity of the injection orifice. The injection potential is defined as the voltage difference between the source flow tube and the injection orifice and was adjusted from 10-100 eV to explore different collision energies ( $E_{\text{lab}}$ ). It should be noted that under these high-pressure conditions, all ions undergo collision and multiple collision events are possible. *Nominal* center-of-mass collision energies ( $E_{\text{cm}}$ ) were calculated using the relation  $E_{\text{cm}} = E_{\text{lab}} \cdot m_{\text{He}} / (m_{\text{He}} + m_{A^-})$  where  $m_{\text{He}}$  and  $m_{A^-}$  are the masses of He and the azolide anion, respectively. The measured CID thresholds were calibrated against the known values for  $\text{CCl}_3^-$  and  $\text{CF}_3^-$  ions, of which the CID experiments were performed under the identical SIFT conditions. An example CID spectrum of imidazolide is shown in the figure below.



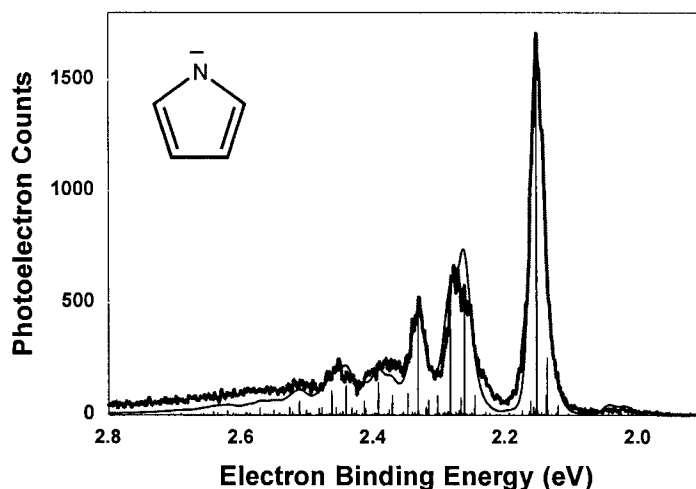
Product distributions were also measured for the CID of these azolide anions as a function of the injection potential. The CID threshold results are summarized below



All of these CID studies take place as we inject ion at a known kinetic energy into the high pressure flow tube. While the collision energy is not cleanly defined here, the ions can confidently be assumed to be quickly thermalized. Thus our studies are very different from the more conventional CID experiments, as, for example, carried out by Armentrout. In order to obtain a better comparison with these single collision CID experiments, Bryan Kilpatrick is carrying out a series of CID measurements of these same ions, but employing an electrospray ionization triple quadrupole mass spectrometer.

## Photoelectron Spectroscopy

In 2003, we reported the photoelectron spectrum of pyrrolide, as shown in the following figure. The spectrum was very regular, and readily fitted with a simple Franck-Condon analysis, giving a  $^2A_2$  ground state and showing no sign of perturbations.

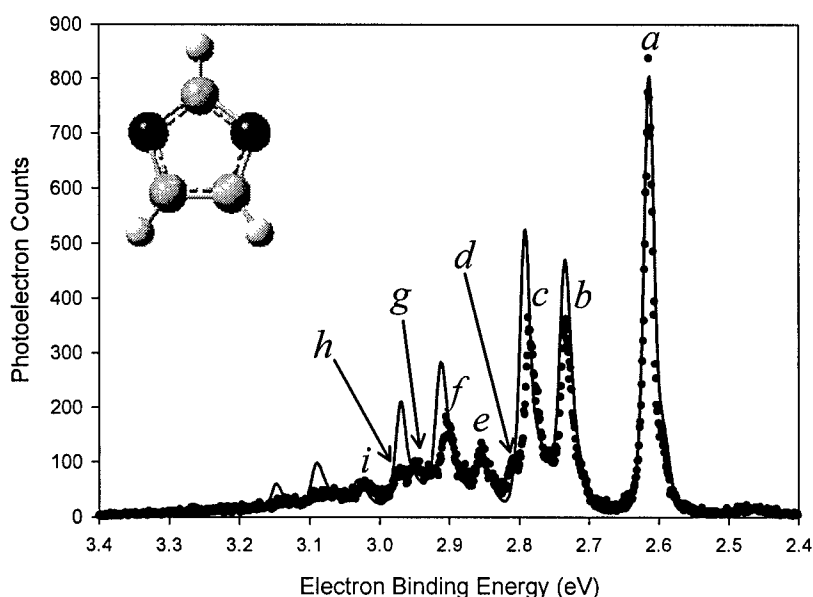


**Figure 1** Photoelectron spectrum of pyrrolide.<sup>12</sup> The red line depicts the experimental data, while the black sticks indicate individual vibrational transitions predicted with the *ab initio* calculations. The blue line transforms the sticks to experimental resolution.

The electron affinity (EA) of pyrrolyl radical has been determined to be  $2.145 \pm 0.010$  eV. Harmonic vibrational frequencies of  $925 \pm 65$ ,  $1012 \pm 25$ , and  $1464 \pm 20$   $\text{cm}^{-1}$  are observed in the spectrum of the  $^2A_2$  ground state of pyrrolyl. As noted, this spectrum is well reproduced by Franck-Condon fitting based on the optimized geometries and the vibrational frequencies of the anion and the radical obtained at the B3LYP/6-311++G(d,p) level of density functional theory (DFT). The observed vibrational modes involve large displacements along the ring coordinates. While the Franck-Condon analysis also predicts a very similar spectrum for the  $^2B_1$  first excited state, only a broad, featureless, weak spectrum is observed near the calculated (2.6 eV) binding energy. The DFT calculations find a transition state for  $^2B_1$  electronic symmetry, as a result of strong vibronic coupling between the  $^2A_2$  and  $^2B_1$  states. The transition state is located very close to a conical intersection of these states. The absence of distinctive features for the  $^2B_1$  transition state in the spectrum arises from the associated lifetime broadening. Using the EA of pyrrolyl together with the N—H bond dissociation energy (BDE) of pyrrole recently determined

by Ashfold, the gas phase acidity of pyrrole was determined to be  $\Delta_{\text{acid}}G_{298}(\text{RH}) = 351.9 \pm 0.4$  kcal mol<sup>-1</sup> and  $\Delta_{\text{acid}}H_{298}(\text{RH}) = 359.4 \pm 0.4$  kcal mol<sup>-1</sup>. The gas phase acidity of pyrrole was also independently determined relative to methanethiol using our tandem flowing afterglow-selected ion flow tube. These measurements now provide a much more accurate set of benchmark acidities for pyrrole and methanethiol, a frequently employed reference acid. This work is described and referenced in full detail in a recent publication<sup>12</sup> in the Journal of Physical Chemistry, and shows the power of this combined experimental/theoretical approach.

Adding a second nitrogen in the 3-position allows formation of the imidazolidine anion, with increased electron binding, but with a photoelectron spectrum that is reasonably straightforward to analyze in terms of single configuration electronic states. The 351 nm photoelectron spectrum is shown below and the analysis is summarized in the following tables. The details of this investigation are ready for publication,<sup>17</sup> and will be submitted within a week.



**Figure 2.** The 351.1 nm magic angle photoelectron spectrum of imidazolidine anion<sup>18</sup>. The points are the experimental data and the blue curve is a 15 meV fwhm Franck-Condon simulation based on the optimized geometries and normal modes obtained from the B3LYP/6-311++G(d,p) calculations.



**Table 1.** Peak positions and assignments for the photoelectron spectrum of imidazolidine.<sup>18</sup>

peak <sup>a</sup>	peak position (cm <sup>-1</sup> ) <sup>b</sup>	assignment <sup>c</sup>
<i>a</i>	0	0 <sub>0</sub> <sup>0</sup>
<i>b</i>	955 ± 15	6 <sub>0</sub> <sup>1</sup>
<i>c</i>	1365 ± 20	3 <sub>0</sub> <sup>1</sup> <sup>d</sup>
<i>d</i>	1575 ± 30	18 <sub>0</sub> <sup>2</sup> <sup>d</sup>
<i>e</i>	1925 ± 25	6 <sub>0</sub> <sup>2</sup>
<i>f</i>	2325 ± 30	3 <sub>0</sub> <sup>1</sup> 6 <sub>0</sub> <sup>1</sup>
<i>g</i>	2695 ± 45	3 <sub>0</sub> <sup>2</sup> <sup>e</sup>
<i>h</i>	2890 ± 55	3 <sub>0</sub> <sup>1</sup> 18 <sub>0</sub> <sup>2</sup> <sup>e</sup>
<i>i</i>	3265 ± 50	3 <sub>0</sub> <sup>1</sup> 6 <sub>0</sub> <sup>2</sup>

**Table 2.** Thermochemical parameters derived for imidazole and imidazolyl.<sup>18</sup>

<i>EA</i> (imidazolyl)	2.613 ± 0.006 eV
$\Delta_{\text{acid}}G_{298}(\text{imidazole})$	342.6 ± 0.4 kcal mol <sup>-1</sup>
$\Delta_{\text{acid}}G_{298}(\text{imidazole})$	342.8 ± 2.0 kcal mol <sup>-1</sup>
$\Delta_{\text{acid}}S_{298}(\text{imidazole})$	23.8 cal mol <sup>-1</sup> K <sup>-1</sup>
$\Delta_{\text{acid}}H_{298}(\text{imidazole})$	349.7 ± 0.5 kcal mol <sup>-1</sup>
$\Delta_{\text{acid}}H_0(\text{imidazole})$	348.4 ± 0.5 kcal mol <sup>-1</sup>
$D_0(\text{imidazole})$	95.1 ± 0.5 kcal mol <sup>-1</sup>
$\Delta_f H_{298}(\text{imidazolyl})$	76.2 ± 0.6 kcal mol <sup>-1</sup>

As the interactions between the nitrogen lone pair electrons increase, single configuration descriptions fail to provide an accurate characterization of the spectrum. Moving one imidazole nitrogen adjacent to the other yields pyrazole, and graphically illustrates this conclusion. We obtained the photoelectron spectrum of pyrazolide anion, preparing pyrazolide by OH<sup>-</sup> deprotonation of pyrazole. Photodetachment from pyrazolide anion leads to the formation of pyrazolyl radical in near-degenerate electronic states. The ground state is assigned as <sup>2</sup>A<sub>2</sub>, with

an adiabatic electron affinity of  $2.939 \pm 0.010$  eV, and the term energy for the lowest excited state ( $^2B_1$ ) is  $0.031 \pm 0.001$  eV. Franck-Condon simulation under the Born-Oppenheimer approximation fails to reproduce the spectrum, indicating strong vibronic coupling in the radical. Coupled cluster calculations have been carried out to evaluate the vibronic coupling constants at the geometry of the pyrazolide ground state. Strong interactions of the pseudo-Jahn-Teller type between the X  $^2A_2$  and A  $^2B_1$  states of pyrazolyl have been found for in-plane asymmetric modes that distort the five-membered ring, analogous to the  $^2E''$  state of an isoelectronic Jahn-Teller system, cyclopentadienyl. While the  $^2E''$  state in cyclopentadienyl is relatively well separated from the  $\sigma$  states, the same is not true in pyrazolyl; interactions with the nearby B  $^2B_2$  state result in further complication of the potential energy surface of the radical. Simulation of the observed spectrum has been attempted with the three-state coupling taken into account. A spectrum has also been measured for deuterated pyrazolide to help with the assignments of the vibronic bands. Here, state-of-the-art electronic structure calculations were essential to obtain qualitatively correct descriptions of the anion and radical. A full paper<sup>20</sup> describing these results, in collaboration with John Stanton (University of Texas) will be submitted by mid-November, 2005.

The studies above benefited enormously from the completion of the new photoelectron imaging spectrometer,<sup>16</sup> which dramatically demonstrated<sup>12</sup> the presence of the broadened transition state in the pyrrolyl radical for  $^2B_1$  electronic symmetry. However, even more important, the azolides containing three or more nitrogen atoms are inaccessible<sup>19</sup> to our standard photoelectron spectrometer. With this new capability, we can obtain spectra of all of the azolides, and also carry out time resolved studies of solvation dynamics.

## Computations

In conjunction with flowing afterglow-selected ion flow tube (FA-SIFT) and negative ion photoelectron spectroscopy (NIPES) experiments in our laboratories, a computational study of the azole family has been carried out.

**Proton Affinity** The proton affinities (PAs) of each of the azoles was predicted at the B3LYP level of density functional theory (DFT) with both the 6-31+G\* and 6-311++G\*\* basis sets

(Table 3). Although both sets of calculations give reasonable values, performing the DFT calculations with the larger basis set appears to give a more accurate value for the proton affinities of the azoles.

Table 3: B3LYP Predicted Proton Affinities

Azole	B3LYP/6-31+G*	B3LYP/6-311++G**	Experiment <sup>a</sup>
	(kcal/mol)	(kcal/mol)	(kcal/mol)
Pyrrole	356.9	359.2	358.6 ± 2.2
Pyrazole	352.7	354.8	353.7 ± 2.1
Imidazole	347.2	349.6	350.1 ± 2.1
1,2,3-Triazole <sup>b</sup>	344.0	346.2	346.4 ± 2.1
1,2,4-Triazole <sup>c</sup>	341.6	344.0	344.2 ± 2.1
Tetrazole <sup>d</sup>	329.3	331.7	333.7 ± 2.1
Pentazole	313.4	315.9	n/a

a) Experimental values from the NIST Webbook (<http://webbook.nist.gov>).

b) Proton affinity of the anion resulting in N-2 protonation. The N-2 protonated neutral is 4.3 kcal/mol more stable than the N-1 protonated neutral at B3LYP/6-31+G\* and 4.2 kcal/mol more stable at B3LYP/6-311++G\*\*.

c) Proton affinity of the anion resulting in N-1 protonation. The N-1 protonated neutral is 6.4 kcal/mol more stable than the N-4 protonated neutral at B3LYP/6-31+G\* and 6.3 kcal/mol more stable at B3LYP/6-311++G\*\*.

**Electron Affinity** The electron affinities (EAs) were also calculated at the B3LYP level of theory with the 6-31+G\* basis set for all of the azoles and the 6-311++G\*\* basis set for all but tetrazole and pentazole. These calculations are much more involved, as many of the azoles have multiple low lying electronic states.

## Personnel

We have benefited from the efforts of several exceptional coworkers. Dr. Shuji Kato has carried out the flowing afterglow ion chemistry and the triple quad collision induced dissociation studies. Dr. Rebecca Hoenigman has carries out the vast majority of the calculations, as well as

synthesizing the pentazole precursors and carrying out the electrospray ionization experiments. Dr. Takatoshi Ichino and Mr. Adam Gianola have carried out the anion photoelectron spectroscopic studies, the detailed analyses, and the investigations of the electronic state couplings that may lead to instabilities. Dr. Jeff Rathbone, Mr. Todd Sanford and Mr. Django Andrews have constructed the photoelectron imaging spectrometer and carried out the first studies of pyrrolide anion.

During the past two years, three new students have joined our efforts, primarily involved with the ion chemistry experiments. Ms. Stephanie Villano has begun PhD studies in the broad area of ion chemistry, and Mr. Bryan Kilpatrick, a graduate of North Carolina Agricultural and Technical Institute, is learning the use of an electrospray ion source and a commercial triple quadrupole mass spectrometer to characterize the various azolide ions. His work on collision induced dissociation will lead to a Master's degree and, hopefully, a PhD degree. Mr. Ryan Calvi has begun research using the photoelectron imaging spectrometer.

### **Interactions/Transitions**

We have benefited from numerous discussions with Dr. Karl Christe and members of his group, as we explore methods to synthesize pentazolide. The pseudo Jahn Teller distortions that may well limit the stability of these compounds raises issues that are being pursued through close contacts with Professors John Stanton, Rod Bartlett and David Yarkony. In addition, we continue to pursue (albeit slowly) studies of silicon carbide clusters and interact with Professor Mark Gordon (Iowa State University) and Professors Larry Burggraf and David Weeks (Air Force Institute of Technology).

a. Invited Presentations at Meetings: August 2002- August 2005

September 6, 2002: MOLEC, Istanbul, Turkey: Photodetachment probes of molecular rearrangement processes

September 28, 2002: APS/OSA Laser Science XVIII meeting: Photodetachment probes of molecular rearrangement dynamics

October 21, 2002: UC Irvine Chemistry Seminar: Organic Radicals, Reactive Intermediates and Transition States: Spectroscopy on the Reaction Coordinate

November 16, 2002: Kyoto University Chemistry Department: Energy flow in ionic clusters

February 9, 2003: Univ. of Minnesota Seminar: Radicals, reactive intermediates and transition states: Spectroscopy along the reaction coordinate

March 4, 2003: Air Force Institute of Technology: Chemistry of silicon carbide clusters

March 17, 2003: North Carolina A&T colloquium: Anion Photoelectron Spectroscopy: Clusters, Free Radicals and Time Evolving States

March 27, 2003: Louisiana State University: Radicals, reactive intermediates and transition states: spectroscopy along the reaction coordinate

April 21, 2003: University of Chicago Closs Lecture: Organic radicals, reactive intermediates and transition states: Spectroscopy along the reaction coordinate.

June 11, 2003: Molecular Beams Conference, Lisbon: Time-resolved dynamics in cluster anions. Solvent reorientation dynamics following electron transfer

July 8, 2003: Univ. Kaiserslautern sonder kolloquium: Dynamics of weakly bound species: electrons to polar molecules and solvents to polar neutrals

July 10, 2003: Heyrovski Institute, Prague: Femtosecond photodetachment probes of molecular rearrangement dynamics

August 17, 2003: Free Radicals Conference, Taipei, Taiwan: Solvated radicals: Spectroscopy along the reaction coordinate

October 7, 2003: Chemistry Seminar, William and Mary University: Photoelectron spectroscopy of organic anions: radicals and reactive intermediates

December 19, 2003: Singapore International Conference on Chemistry, December: Asymmetry Counts: The importance of asymmetric solvation

January, 2004: Noyes Distinguished Lecture, University of Texas: Radicals, Reactive Intermediates and Transition States: Spectroscopic studies of the reaction coordinate

March, 2004: Debye Award lecture, ACS Annual Meeting: Anion photochemistry: free radicals, clusters, and time evolving states

April, 2004: Faraday Discussion, Oxford University: Energy Flow in Ionic Clusters

May, 2004, AFOSR Contractor Meeting, Newport, RI, Nitrogen-rich heterocycle thermochemistry

June, 2004: G. W. Flynn symposium, Columbia University: Solvent dynamics

August 2004, 27<sup>th</sup> International Symposium on Free Radicals, Taipei, Taiwan: Solvated radicals: spectroscopy along the reaction coordinate.

August 2004: W. P. Reinhardt Telluride Symposium, August: Energy flow ala Reinhardt

October 15, 2004: Laser Analysis and Probing Conference, Argonne, IL: High resolution photoelectron imaging spectroscopy of anions

January, 2005: Gordon Conference on Molecular Energy Transfer, Ventura, CA: Time resolved energy flow in size-selected cluster anions

February, 2005: Gordon Conference on Gaseous Ions, Santa Barbara, CA: Energy Flow in Cluster anions

March, 2005: U. Cal. Berkeley Chemistry Seminar: Time Resolved energy flow in size-selected cluster ions

March, 2005: Zare Nichols Award Symposium, White Plains, NY: Photoelectron spectroscopy of anions

July, 2005: Femtochemistry Conference, Washington, DC: Time resolved energy flow in size-selected cluster anions

August 2005: Pinhead Institute Summer Toen Extravaganza Lecture, Telluride, CO: Lasers – the light fantastic!

b. Consultative and Advisory to laboratories and agencies.

Carl Lineberger is heavily involved with a science policy and advice at the national level. In September, 2003, he served as a special member of the Air Force Scientific Advisory Board, participating in a review of the Air Force Office of Scientific Research. His current advisory positions include the following:

1. Member, Council of the National Academy of Sciences
2. Member, Governing Board, National Research Council
3. Member, Committee on Science, Engineering and Public Policy, National Research Council
4. Chair, Mathematical and Physical Sciences Advisory Committee, National Science Foundation

### **Inventions and patent disclosures**

There have been no inventions leading to patent disclosures during the period of this grant.

### **Papers Published**

We have published or submitted a number of papers concerning ion dynamics and energetics during this grant period. The following papers have wholly or partially benefited from AFOSR support.

1. "Photoelectron spectroscopy of nickel, palladium, and platinum oxide anions," *J. Mol. Spectrosc.*, **216**, 1-14 (2002), T. M. Ramond, G. E. Davico, F. Hellberg, F. Svedberg, P. Salén, P. Söderqvist and W. C. Lineberger.
2. "The heat of formation of the hydroperoxyl radical HOO via negative ions," *J. Phys. Chem.* **106**, 9641-47 (2002), T. M. Ramond, S. J. Blanksby, S. Kato, V. M. Bierbaum, G. E. Davico, R. L. Schwartz, G. B. Ellison, and W. C. Lineberger.
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## Honors/Awards

In March, 2004, W. Carl Lineberger was awarded the 2004 Peter Debye Prize in Physical Chemistry, given by the American Chemical Society.

### Lifetime Achievement Awards

National Academy of Sciences, 1983

American Academy of Arts and Sciences, 1995

Fellow, American Physical Society

Fellow, American Association for the Advancement of Science

Herbert P. Broida Prize in Chemical Physics, American Physical Society, 1981

Bomem-Michelson Prize, Coblentz Society, 1987

William F. Meggers Prize, Optical Society of America, 1988

Phi Beta Kappa National Lecturer, 1989

Earle K. Plyler Prize in Molecular Spectroscopy, American Physical Society, 1992

Irving Langmuir Prize in Chemical Physics, American Chemical Society, 1996

Peter Debye Award in Physical Chemistry, American Chemical Society, 2004